A PROLONGED, LARGE SCALE, OFF-SEASON PHOTOCHEMICAL OXIDANT EPISODE

by

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ABSTRACT

Oxidant concentrations exceeding 160 μ g/m³ were observed at many locations in a 7-county area in southern California from February 25 to March 4, 1975. Because this was a violation of the air quality standard at a time when relatively low concentrations were normally anticipated the meteorological conditions associated with this large scale episode were evaluated. A more complete understanding of the meteorology associated with the episode should provide a better background for devising an abatement strategy. The episode was associated with very slow air movement, slightly elevated temperatures, abundant solar radiation, limited vertical mixing at the coast, and vertical mixing varying from negligible at night to relatively deep in the daytime at inland sites. The maximum temperatures were 3° to 6°C cooler than those normally associated with high oxidant concentrations, but the solar radiation, as deduced from sky cover and sunshine records, was about equivalent to that at the end of the usual oxidant season. The differences in vertical mixing, combined with the overall stagnation and weak sea breeze at the surface in the afternoon, appeared to cause the oxidant concentrations to be higher inland.

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INTRODUCTION

The concentration of photochemical oxidant (POX) is considered a problem when it exceeds the hourly National Ambient Air Quality Standard (NAAQS) of 160 $\mu g/m^3$ or 8 pphm¹. In California POX is measured as total oxidant* and ozone, and the typical months of high POX concentrations are usually considered to be May through October^{3,4}. The reasons suggested for the nonoccurrence of high concentrations in the cool half of the year are that the temperatures are not high enough and the solar radiation is insufficient for substantial oxidant formation. However, a quarterly summary of the California Air Resources Board shows that during the period of February 25 through March 4, 1975, a large number of stations in 7 counties in southern California recorded concentrations which violated the standard. Since a more complete knowledge of the meteorology associated with these high concentrations could aid in the formation of an improved abatement strategy, this investigation was undertaken to obtain that knowledge. The meteorological conditions associated with the episode are examined and summarized to suggest which phenomena appeared to contribute to the high concentrations. The temperature and radiation observations of the period are compared to those of the POX season. In addition, special consideration is given to the temporal and spatial variation of the bases and tops of inversions as shown by the vertical soundings made at Los Angeles Airport and El Monte⁵.

^{*}Specific spectroscopic measurements indicate ozone is the principal oxidant in California air².

CONCLUSIONS

On the basis of the analyses of the February 25 to March 4, 1975 southern California data, the following conclusions are drawn:

- This prolonged period of high POX concentrations occurred at a time when high concentrations were not a normal occurrence.
- 2. The episode was associated with stagnation, slightly elevated temperatures, abundant sunshine, limited vertical mixing at the coast, and vertical mixing varying from negligible at night to relatively deep in the daytime at inland sites.
- 3. The maximum temperatures were about 3° to 6°C cooler than those normally assciated with high POX concentrations, but the radiation, as deduced from the NO_2 photodissociation rate constant, k_1 , was about equivalent to that at the end of the usual POX season (about 11 hours duration and a maximum rate constant of 8 x 10^{-3} per second).
- 4. The differences in vertical mixing combined with the overall stagnation and weak sea breeze at the surface in the afternoon appeared to cause the POX concentrations to be higher inland.

BACKGROUND AND METHODS

OZONE AND TOTAL OXIDANT MONITORING STATIONS AND THE DATA

The southern California area has a large network of ozone and total oxidant monitoring stations. Although the total oxidant monitors react to nitrogen dioxide and organic peroxides, ozone is the principal oxidant in California air². All of the total oxidant monitors in southern California are colorimetric instruments and are standardized against ozone. The ozone concentrations are determined by instruments utilizing one of two physiochemical processes: non-dispersive ultraviolet absorption or chemiluminescence. Both types of instruments are calibrated using known constant ozone standards².

A special note is needed here because of a change in the recording of POX values in California. There was a discrepancy in the POX values recorded by the Los Angeles Air Pollution Control District and the other control agencies. All POX data collected beginning June 1, 1975 are comparable and to make all prior data comparable, the reported non-Los Angeles County data are to be multiplied by 0.8⁶. Accordingly, all non-Los Angeles County data in this report have been made comparable.

The locations of the ozone and total oxidant stations are shown in Figure 1. Many stations record both ozone and total oxidant, and several cities have more than one station. The interest in this study is the highest concentration of POX for each day without regard to whether it was observed as ozone or total oxidant. In the presentations that follow, only the highest hourly concentration is Shown, and ozone and oxidant are used interchangeably with each other and with POX.

METEOROLOGY PREVIOUSLY ASSOCIATED WITH HIGH POX CONCENTRATION

The meteorological conditions associated with high POX concentrations in southern California have been documented in many investigations $^{6-17}$. The earliest study 7 correlated high concentrations of POX with weak winds and

stagnant air. Other early comprehensive investigations 8-11 related variations in ozone concentrations to variations in the following: intensity and duration of solar radiation; surface temperature; the depth of the polluted layer (the top coincided with the base of the subsidence inversion); and wind speed and direction. In these early studies high concentrations were considered local, low-level problems. However, following the report 12 that winds aloft are important in transporting "second-hand" ozone to unsuspecting downwind areas, investigators examined the three-dimensional picture and long-range transport phenomena. Evidence 13,16 confirms that high POX concentrations are frequently in the air aloft, even within the subsidence inversion, and that the locations of these contaminated layers aloft are determined by the winds aloft. Eventually, parts of the contaminated layers are brought to the surface in daytime mixing. Other studies 17,18 have shown that the highest ozone concentrations occur with heat waves. Finally, although some investigations 19,20 have indicated that stratospheric ozone may contribute to high surface ozone concentrations in other places, no similar finding has been reported for southern California.

METEOROLOGICAL DATA

The surface weather observations ^{21,22} in this report are from the following stations: Burbank Airport, Los Angeles International Airport, Los Angeles Civic Center, Ontario Airport, Riverside Airport, Norton Air Force Base (San Bernardino), and San Diego International Airport. The meteorological parameters summarized are: the daily maximum and minimum temperatures, the prevailing wind direction and average speed for each quarter-day, the percent of possible sunshine for each day, sky condition for each day and weather (obstructions to visibility, precipitation) that occurred during the day.

Discussions of the synoptic conditions are based on the Daily Weather Map 22 and the daily resumes 5 of the National Weather Service Air Pollution Forecaster in Los Angeles. The Daily Weather Map is used to locate high and low pressure areas and fronts. The Daily Weather Map shows two maps for each day based on 4 a.m. (all times are Pacific Standard) observations; one map is the surface and the other for 500 millibars (mb) (about 5500 meters (m) apove the surface).

Special attention is given to solar radiation data with emphasis on the

photodissociation rate constant, k_1 , for nitrogen dioxide, NO_2 . This constant is explained in detail by Leighton²⁴. Ozone production in the presence of ozone precursors is directly related to the value of k_1 .

A second phenomenon given special consideration is the time and spatial variation of the bases and tops of inversions. Records 5 from the National Weather Service show that a variation does exist which may partially account for higher concentrations in the eastern part of the Los Angeles basin.

RESULTS

POX CONCENTRATIONS

The highest hourly POX value for each day for each station is shown in Figures 2 through 9.

On February 25 (Figure 2) there were violations of the standard (8 pphm) in all 7 counties. Most coastal areas had concentrations at or just below the standard, whereas at the inland locations concentrations generally were higher than the standard by 25 to 75 percent.

On February 26 (Figure 3) the only coastal city with a violation was Chula Vista in San Diego County and 4 inland cities--Newhall, Temple City, Upland, and Fontana--had concentrations which were twice as high as the standard.

On February 27 (Figure 4) the coastal stations just below Los Angeles had low concentrations whereas El Toro and the coastal stations in San Diego had violations. Inland, 7 stations recorded concentrations twice the standard and several exceeded 400 $\mu g/m^3$ (20 pphm).

On February 28 (Figure 5) the only areas without violations were on the immediate coast and areas within 16 km of the coast had readings ranging from 200 to 420 $\mu g/m^3$ (10 to 21 pphm). Inland the average concentrations were about twice the standard and a violation was noted at Victorville in the desert to the north as well as at Palm Springs in the eastern desert.

On March 1 (Figure 6) violations occurred throughout the 7-county area with the coast being relatively clean and inland areas badly contaminated.

On March 2 (Figure 7) violations were reported in only 4 counties, the coast was relatively clean, and inland the concentrations were lower than they were on March 1.

On March 3 (Figure 8) the concentration pattern was similar to that of March 2, but fewer stations recorded violations, 20 versus 17.

On March 4 (Figure 9) only 2 violations occurred in northwest Los Angeles County and 1 occurred in eastern Orange County. Large parts of Western San Bernardino and Riverside counties had violations.

SURFACE WEATHER OBSERVATIONS

The maximum temperatures at the 7 stations (Table 1) reveal that the period averaged slightly warmer than the long term average at the coast, while inland it was 3° to 6°C warmer than average. However, these temperatures were about 6° to 8°C colder than those of July. These maximum temperatures show the normal condition of marked increase from the coast inland. Los Angeles Airport had temperatures around 15°C while Ontario and San Bernardino had temperatures in the range of 26° to 32°C (80's°F). These higher temperatures inland indicate that such locations had vertical mixing to considerably greater heights than the coastal locations.

The diurnal range of temperature (today's maximum minus tomorrow's minimum) shows where radiation inversions likely form at night; when the range is 14°C or greater at a location in southern California there is a very high probability that nocturnal surface-based inversions form²⁵. These maximum-minimum temperature ranges in Table I indicate that inland locations must have had nocturnal inversions almost every night while coastal areas did not have these surface-based inversions. The Los Angeles and El Monte data, which are limited to the workweek days and are presented in a following section, showed that the coast generally did not have surface-based inversions while El Monte did have them. The periods of warming and cooling, particularly at inland locations, were neither associated with increases and decreases in concentrations nor expansion and contraction of the affected areas.

The winds were generally light except during the third quarter of each day. During this afternoon period, there was a sea breeze flow with a general west-to-east movement, except at Burbank where a sea breeze comes out of the south-southeast.

The two sunshine records reveal that the coastal area had two-thirds or more of the possible sunshine on each of the first 7 days; on the eighth day the sunshine was markedly less.

The sky conditions (as well as the temperatures) at the inland stations indicate that they had greater amounts of sunshine than the coastal sites. Smoke and haze were consistently present after the first day. At the 4 successive downwind stations, Burbank, Ontario, San Bernardino, and Riverside, the smoke and haze were dense enough to partially obscure the sky; the visibility generally was less than 5 km at these stations.

The overall indication was that the episode was not associated with particularly high temperatures; there was slow moving air; the sunshine was abundant; inland, there was limited nocturnal vertical mixing and relatively deep daytime mixing; and obscuring phenomena tended to stay in the area.

The higher concentrations at inland than at coastal locations are assumed to have been due, partially, to differences in vertical mixing. The typical diurnal air movement shows ozone and its precursors being carried inland with the sea breeze 14 in the daytime while a weaker reverse flow exists at night. The wind directions at Los Angeles, Ontario, and Burbank indicate that this diurnal flow occurred during this period (Table 1). In the daytime, the more polluted air (Figures 2-9) that was inland was dispersed by vertical mixing through deeper layers than the polluted air in coastal areas. Then, at night, there was a reverse flow and in the eastern areas radiation inversions formed (Figure 11), cutting off mixing between the surface and layers aloft. Since the ground is a sink at which ozone is destroyed 26, a contrast was set up between inland areas and the coast. Inland the ozone aloft remained intact, except for scavenging by the NO present in that layer. At the coast, vertical mixing continued through the night and the relatively shallow ozone reservoir aloft was diluted by mixing with the surface air; part of the ozone was destroyed at the surface so the concentrations aloft and at the surface decreased with time. The cleansing was augmented by having relatively clean air advected in with the drainage winds from inland areas; these drainage winds had little or no contact with the ozone aloft and the operations of the sources of precursors (primarily autos) inland were greatly reduced. In the following daylight periods during the first few hours, the emissions of precursors increased tremendously throughout the Basin and the sea breeze winds mo. I the air eastward. The abundant sunlight (Table 1) reacted with the precursors to produce ozone. The coastal areas had few upwind sources and

they had relatively low concentrations while areas inland had high concentrations. As the day progressed both the coastal and inland areas had their surface air mixed with the air aloft. The coastal areas had a relatively small amount of ozone with which to mix while inland areas had a deep layer with high concentrations of ozone. This gradient aloft, from inland to the coast, although not documented on this occasion, has been documented on other occasions when similar meteorological conditions prevailed 13. Thus the inland areas had high concentrations due to the combined effects of advection and the mixing downward of ozone from aloft. In periods of slow air movement, this source of "second-hand" ozone, coming from aloft, adds to the ozone problem associated with surface advection.

DAILY WEATHER MAPS

The 500-mb maps for February 25 through March 3 generally showed a weak, flat ridge over or a little to the east of California. This condition ended on March 4 when an upper level low with cool, moist air moved into California. The surface maps showed pressure gradients which allowed a very weak onshore flow from February 25 to March 3. Weak cold fronts or troughs moved through the area early on February 27 and March 2. On March 4 there was a moderate onshore gradient; rain fell on some areas of southern California.

SPECIAL SOLAR RADIATION DATA

Since an episode developed during February 25 through March 4, it is concluded that the solar radiation was sufficient for generation of significant ozone concentrations. According to the weather observations, the indication is the radiation was intense for this time of year. No direct measurements of solar radiation were made so an alternate method of evaluating the radiational effects had to be employed. Because the NO₂ photodissociation rate constant, k_1 , is a key factor in ozone generation 24 , data on the temporal variation of k_1 were sought. A new method 27 for calculating the diurnal variation of k_1 for clear sky conditions (the prevailing situation) was used for June 21 and December 21, the seasonal extremes, as well as for the midday of the episode, March 1. The results are shown in Figure 10. The values of k_1 on March 1 are considerably smaller than those of June 21, but markedly greater than those of December 21. On June 21 photodissociation starts around

5 a.m. and ends about 6:45 p.m. whereas on March 1 the starting time is about 6:45 p.m. and ending time 5:30 p.m.; the photodissociation occurs for 3 hours longer on June 21. Table 2 shows the ratio of the on-the hour values of k_1 for March 1 versus those for June 21. Only during the middle of the day are the March 1 values 80 percent of those of June 21. The overall indication is that the photodissociation can be considerably reduced from the extreme value and duration, yet still be sufficient to generate high ozone concentrations. In absolute values and durations, a maximum k_1 of $8 \times 10^3 \, {\rm sec}^1$ and a duration just short of 11 hours seems sufficient when other conditions are right. Although the days in this episode are cold-season days, the radiation results are not surprising. March 1 is comparable to October 10 with regard to elevation angle of the sun and radiation, and October 10 is considered to be near the end of the season with high ozone concentrations $2\cdot3$. (Note: The maximum temperatures, when compared to October 10 averages, were about 6° C colder on the coast and 3° C colder inland.)

TEMPORAL AND SPATIAL VARIATION OF BASES AND TOPS OF INVERSIONS

The heights and temperatures of the bases and tops of inversions indicate the potential for vertical mixing. When the bases are low and the temperature differences between the bases and tops are large, there generally is limited vertical mixing. When the bases are high or the temperature differences are small (that is, the inversion is easily eliminated with additional heating), vertical mixing can be extensive. In the Los Angeles area data on the heights and temperatures of the bases and tops of inversions are provided twice a day, 6 a.m. and noon, Monday through Friday, for 2 sites, Los Angeles Airport (near Lennox) and El Monte (close to Temple City), by the National Weather Service²³. A graphical presentation of these data for February 25 through March 4 is shown in Figure 11. The Los Angeles Airport, a coastal location, usually observed inversions with elevated bases and temperature differences exceeding 3.0°C (considered large and not easy to eliminate when observed at $noon^5$). The elevated bases were 460 m or lower most of the time and the inversions remained intact and intense through the daytime; relatively rapid vertical mixing occurred continually throughout the 24-hour day, but was limited. At El Monte, an inland station, most of the 6 a.m. inversions were surfaced-based, indicating that vertical mixing was very slow and limited at

night. At noon over El Monte the inversions were weak (averaging 1.0°C).and probably eliminated in the afternoon; vertical mixing had no inversion lid. Normally, this better daytime vertical mixing inland would mean greater dilution by mixing with a larger volume of clean air aloft. However, the winds aloft up to about 900 m from February 25 through March 3 were light and variable⁵, indicating very slow movement aloft. It is well-documented 11,12,13 that ozone buildup occurs during periods with sluggish air movement aloft and that the layers aloft can be the source of "second-hand" ozone brought down to the surface by vertical mixing. The "second-hand" ozone might have been a major contributing factor to the extremely high concentrations observed at stations in the vicinity of El Monte.

SUMMARY

- 1. During the cool part of the year when high POX concentrations do not normally occur, there was an 8-day period when a 7-county area in southern California experienced a POX episode.
- 2. The episode was associated with stagnation; the winds at the surface and aloft were light. At the surface, there was a very weak land breeze at night and during the day an organized onshore flow.
- 3. The episode was associated with relatively warm temperatures and intense radiation for the season. (as deduced from sky cover and sunshine records). The maximum temperatures were considerably lower than those which occur during the peak POX season and even 3° to 6° C lower than those which occur at the end of the POX season in the fall. The radiation, as shown by the photodissociation rate, k_1 , for NO_2 , was considerably less than that observed at the height of the POX season, but similar to that at the end of the normal POX season.
- 4. There was a marked difference in the vertical mixing at the coast and inland. Vertical mixing was continuous, but limited throughout the 24-hour day at the coast, while inland there was negligible mixing at night and relatively deep mixing in the daytime.
- 5. The differences in vertical mixing may have accounted, in part, for the differences in the severity of the problem. The higher concentrations occurred inland where vertical mixing during the daytime brought down oxidant from the previous day that had been trapped aloft. Each day more POX was added near the surface, and there was no clean air aloft with which to dilute the surface concentrations. At the coast vertical mixing allowed for a relatively uniform vertical distribution of POX, which enhanced destruction at night near the surface. Additionally, the coastal area benefited from the organized afternoon fl_{V} 3 at the surface that brought relatively clean air to the coast.

Simultaneously, the inland areas were having high concentrations of ozone advected in from the coast and brought down from aloft; the ozone problem inland was compounded.

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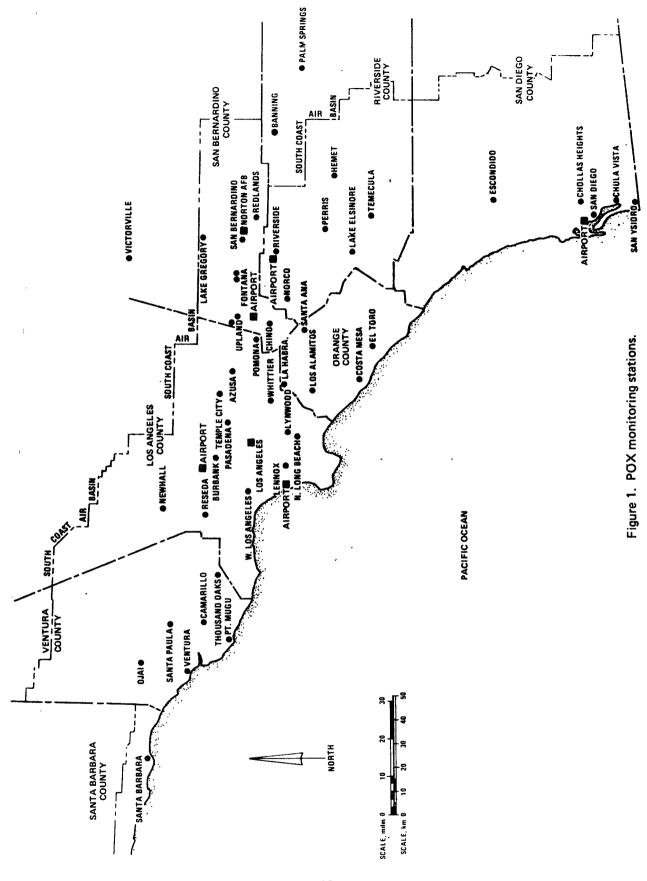
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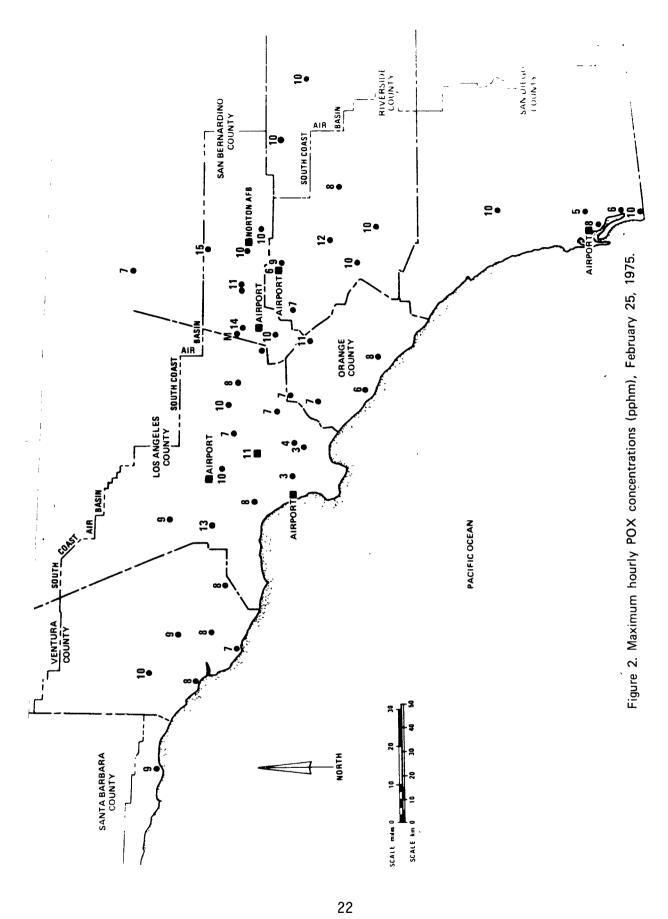
TABLE 1. METEOROLOGY DURING EPISODE OF FEBRUARY 25 TO MARCH 4, 1975

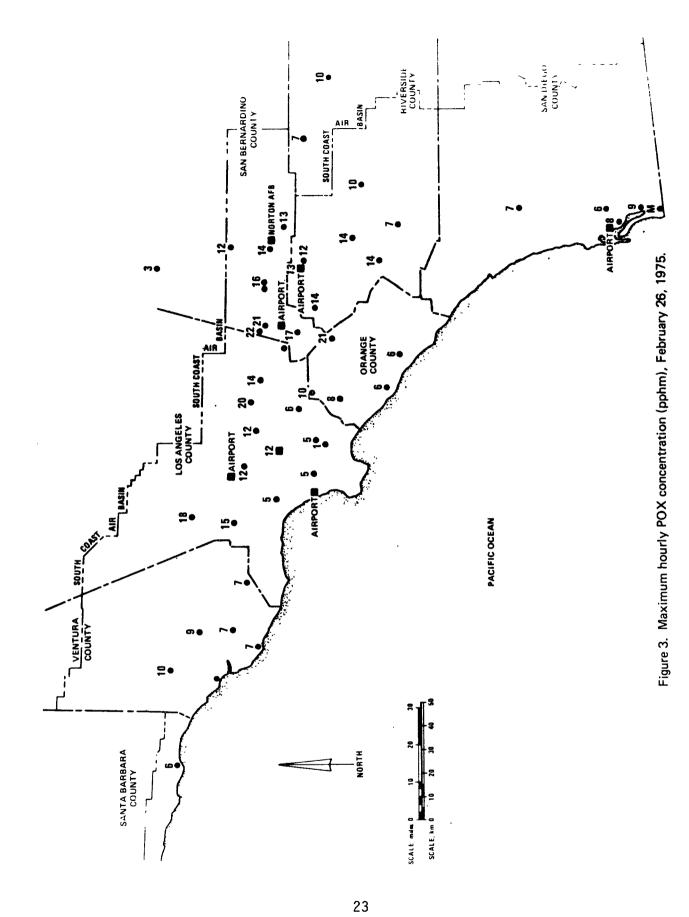
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Ontario Airport								
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Avg, Speed (mps) Sky Condition Weather	4 2 5 3 CLEAR K,H	3 4 08S F,К,Н	3 2 4 3 08S F,K,H	3 0BS F,K,H	7	6 2 4 6 08S 8 3 8 8 9 8 9 9 9 9 9 9 9 9 9 9 9 9 9 9	3 2 5 3 08S F,K,H	3 2 3 3 08S 4.K.H
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Avg. Speed (mps) Sky Condition Weather	S CLEAR K,H	0ВS F, К, Н	08S F,K,H	. 08S K,H	, 0BS F, K, H	08S F,K,H	CLEĂR K,H	08S F,K,H

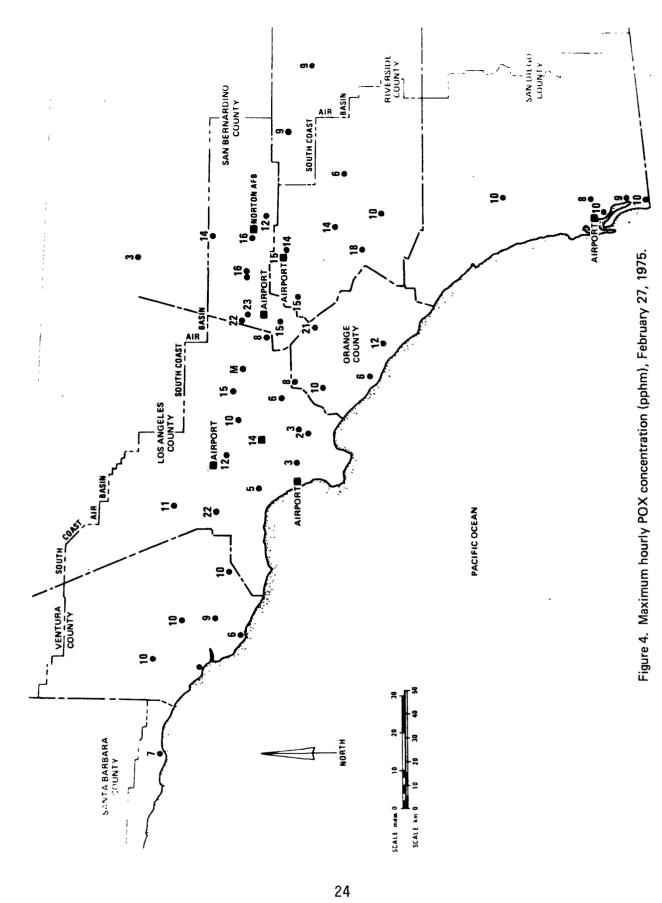
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19	Notes:			,	ν]	Symbols and Abbreviations:	: ions:		
	WD, WS= Wind direct	ton and spe	ed for each co	WD,WS= Wind direction and speed for each consecutive quarter-day.		T≖ Temperature		CLDY= Cloudy	
	1-Max and Min temp	eratures de	termined from	i-Max and Min temperatures determined from hourly observations	ပ	C= Calm		OBS= Obscuration	
	2-Observations taken from 5 a.m. to 9 p.m. only	en from 5 a	.m. to 9 p.m.	only	>	VAR= Variable		F= Fog	
					S	SCTD= Scattered Clouds		K= Smoke	
					G.	PTLY= Partly Cloudy		H= Haze	
						,			

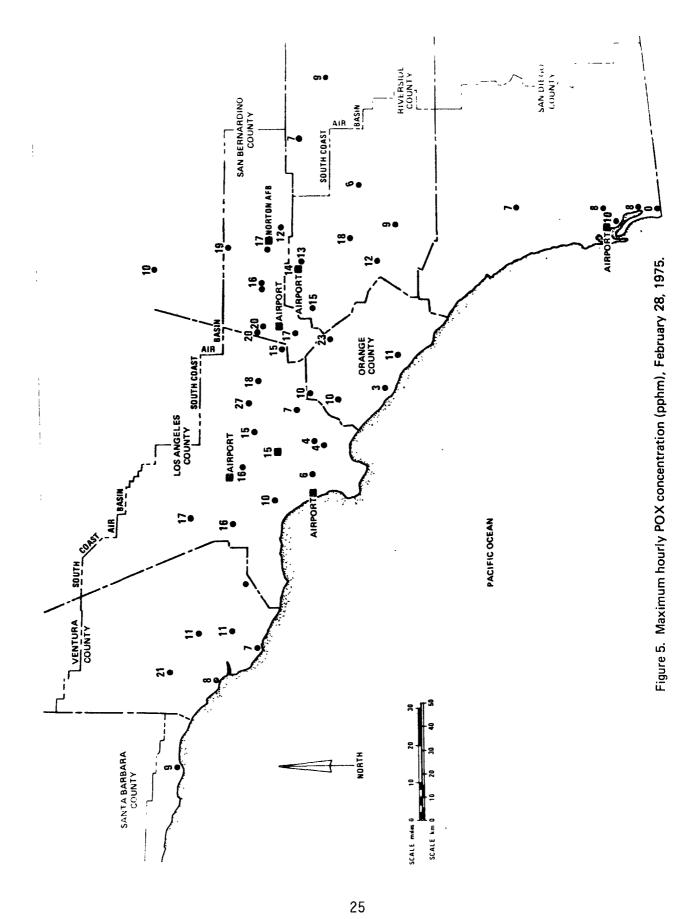
TABLE 2. VALUES	OF k ₁ FOR MAR	CH 1 DIVIDED BY k	FOR JUNE 21
7 a.m.	0.17	1 p.m.	0.84
8	0.49	2	0.82
9	0.70	3	0.76
10	0.79	4	0.59
11	0.83	5	0.28
Noon	0.85	6	-

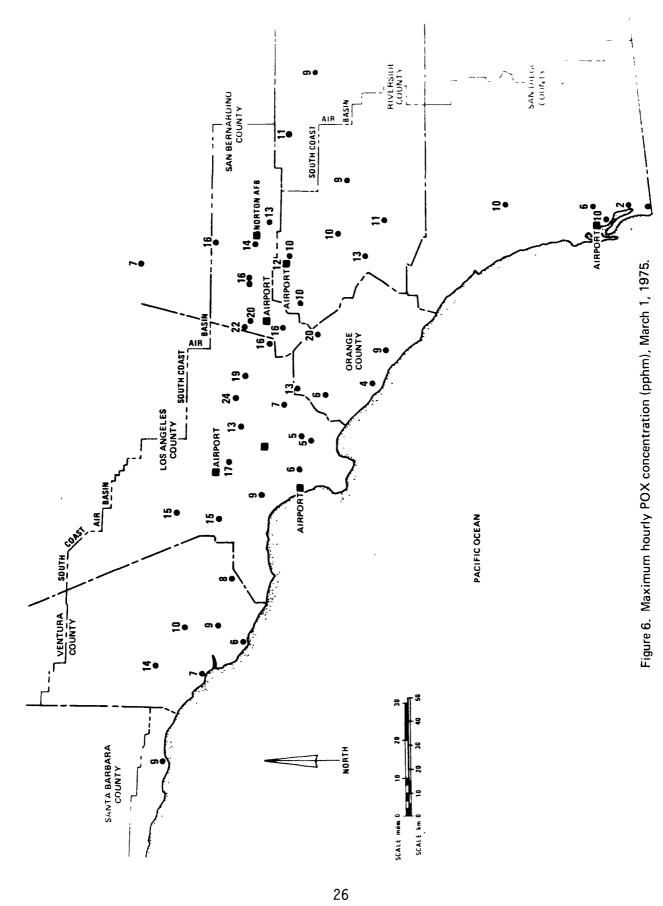


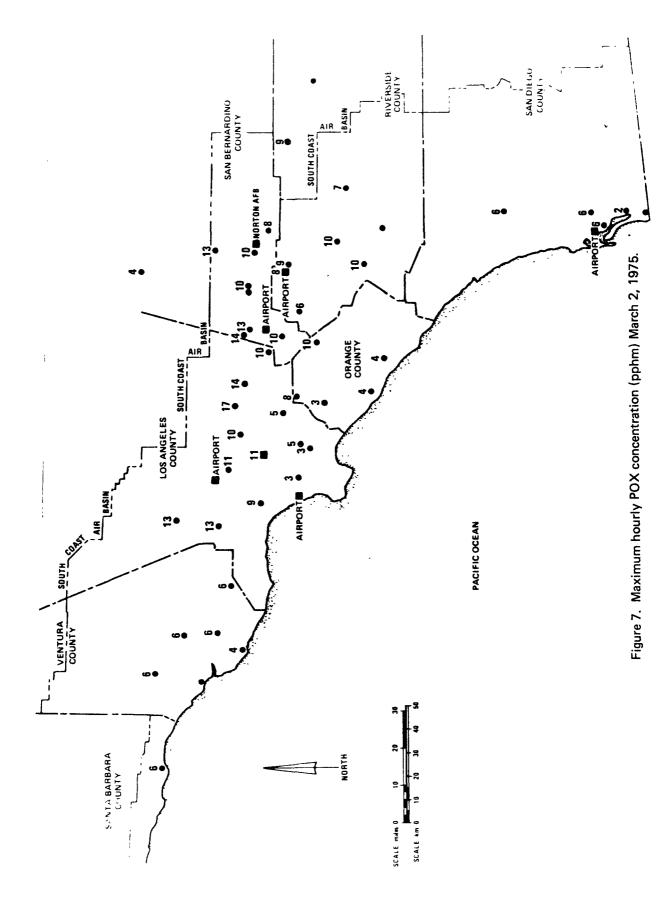












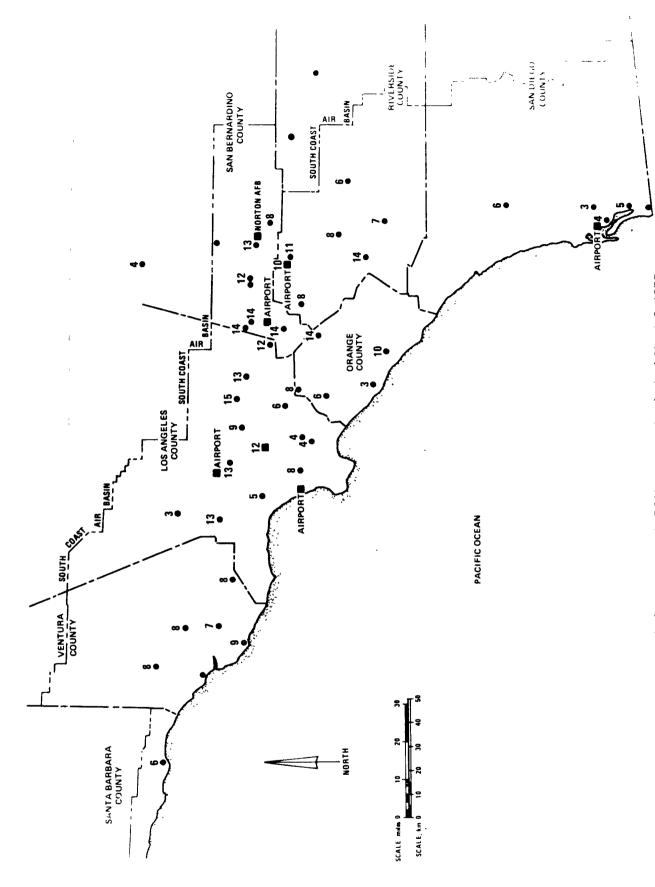
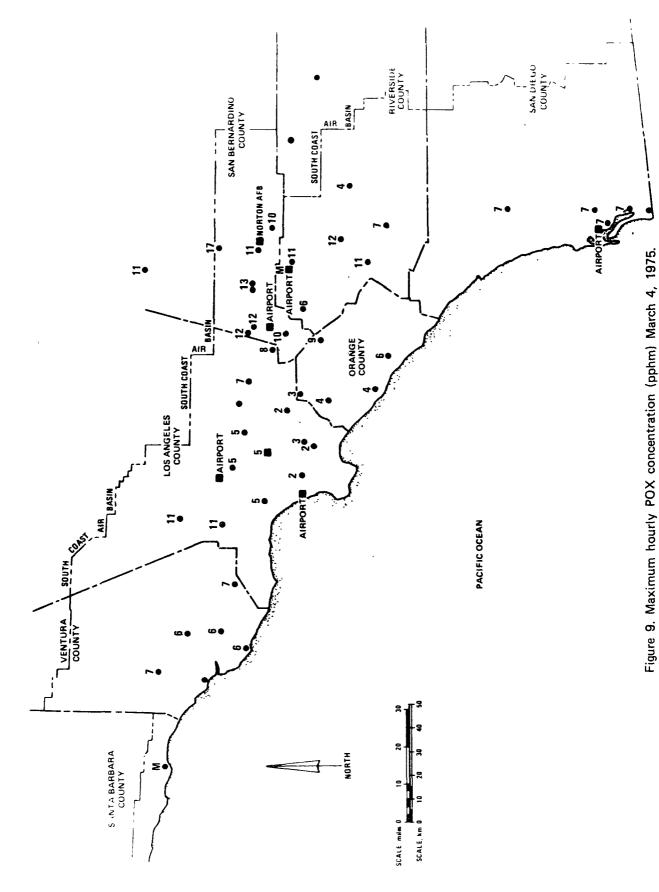


Figure 8. Maximum hourly POX concentration (pphm) March 3, 1975.



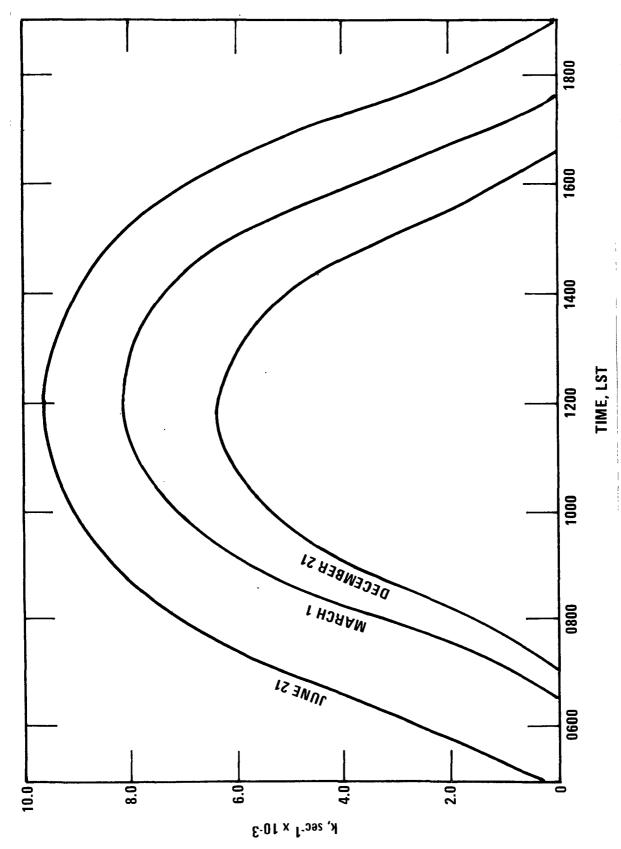


Figure 10. Diurnal, clear sky values of k. The photodissociation rate constant for NO2 for Los Angeles (34.1°N, 118.3°W).

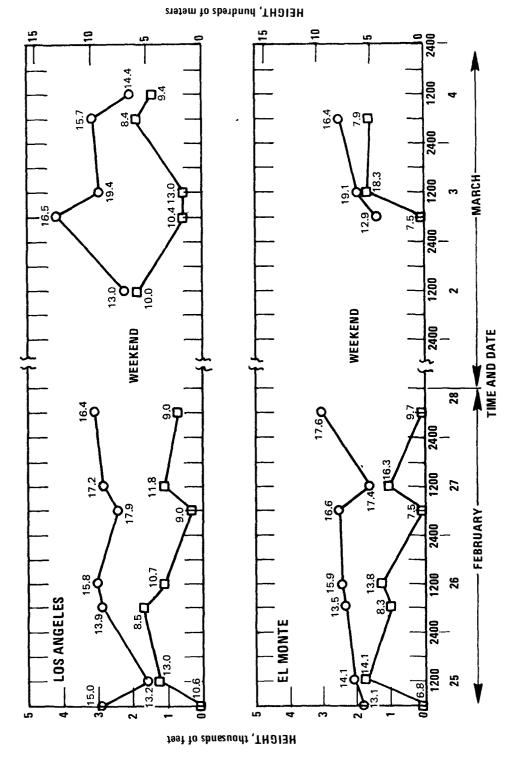


Figure 11, Variation of height and temperature (°C) of bases (0) and tops (0) of inversions.

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15. SUPPLEMENTARY NOTES

*On assignment from the National Oceanic and Atmospheric Administration, U.S. Department of Commerce.

16. ABSTRACT

Oxidant concentrations exceeding 160 µg/m³ were observed at many locations in a seven-county area in southern California from February 25 to March 4, 1975. Because this was a violation of the air quality standard at a time when relatively low concentrations were normally anticipated, the meteorological conditions associated with this large scale episode were evaluated. A more complete understanding of the meteorology associated with the episode should provide a better background for devising an abatement strategy. The episode was associated with very slow air movement, slightly elevated temperatures, abundant solar radiation, limited vertical mixing at the coast, and vertical mixing varying from negligible at night to relatively deep in the daytime at inland sites. The maximum temperatures were 3° to 6°C cooler than those normally associated with high oxidant concentrations, but the solar radiation, as deduced from sky cover and sunshine records, was about equivalent to that at the end of the usual oxidant season. The differences in vertical mixing, combined with the overall stagnation and weak sea breeze at the surface in the afternoon, appeared to cause the oxidant concentrations to be higher inland.

7. KEY WO	KEY WORDS AND DOCUMENT ANALYSIS .				
. DESCRIPTORS	b.IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group			
* Air pollution* Ozone* Meteorological data* Evaluation	Southern California	13B 07B 04B			
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